



ED37713559445

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: Douglas E. Fain, Sr., et al. :
SERIAL NO.: 10/611,743 : Art Unit: 1762
FILED : 06/30/03 : EXAMINER: Eric B. Fuller
FOR: ARTICLE AND METHOD FOR PRODUCING EXTREMELY
SMALL PORE INORGANIC MEMBRANES

DECLARATION UNDER 1-1.32

Roddie R. Judkins declares and says that has a Bachelor of Science Degree in Engineering Chemistry (1963) and a Masters of Science Degree in Chemistry from Tennessee Polytechnic Institute, now Tennessee Technological University (1965), and Doctor of Philosophy Degree in Physical Chemistry from the Georgia Institute of Technology (1970);

That he has and continues to work as a researcher in the technical field of fossil energy, which includes inorganic membrane technology, holding the following positions of responsibility:

- Plant Manager, Nuclear Chemical and Metals corporation;
- Vice President and Technical Associate, E.R. Johnson Associates Nuclear Audit and Testing Company; and
- Manager of Fossil Energy Programs, Oak Ridge National Laboratory UT-Battelle L.L.C., the Management and Operator Contractor for the Department of Energy, Oak Ridge, TN

That he has held the position of Fossil Energy Program manager and/or director for over 19 years and has in that management position also for the last 17 years had technical oversight for the Inorganic Membrane Technology Laboratory at the Oak Ridge National Laboratory;

That in that position he is cognizant of the technical field of inorganic membranes, including zeolites and other similar molecular sieves such as ALPO, SAPO and MCM41;

That these membrane materials are generally characterized by extremely small pores of molecular dimensions and fairly uniform size, e.g., on the order of <1.0 nm ($<10\text{\AA}$) and have the ability to adsorb and/or pass small molecules but not large ones;

That he has read and is familiar with patent application Ser. No. 10/611,743, filed in the names of Douglas E. Fain, Sr., et al, for "Article and Method for Producing Extremely Small Pore Inorganic Membranes:"

That he is aware of and has read the Office Action dated October 4, 2005, issued by Examiner Eric Fuller of the U.S.P.T.O. in the above-identified patent application,

That he has carefully read and understands the Funke et al., Butler et al. and the Levy et al. patents cited by the Examiner against Applicants' claims 2-24;

That in particular with reference first to the Funke et al. and Butler et al. patents he understands that the Examiner rejected Claims 2-24 under 35 U.S.C. 103(a) as being unpatentable over Funke et al. in view of Butler et al.;

That he has read and understands Applicants' response (Amendment B) to the Office Action dated May 26, 2005, and in particular Applicant's arguments made that Funke et al. teaches to apply the monolayers to the surface of the membrane and alleges that this fails to teach the claimed invention;

That he notes in particular Examiner's statement in the Office Action dated October 4, 2005, that this is not found convincing and further that the Examiner went on to say that since Funke et al. explicitly teaches to reduce the diameters of the pores of the membrane with the reactant, the surface that Funke et al. is concerned with must be the surface of the pore walls and this reads on Applicants' claims;

That further he notes that the Examiner also stated that Funke et al. teaches that the membrane may be a zeolite or any other inorganic membrane that has surface hydroxyl groups;

That with respect to the Examiner's statements that (1) the surface that Funke et al. is concerned with must be the surface of the pore walls and (2) that Funke et al. teaches that the membrane can be any other inorganic crystalline membrane, the statements are believed to be in error as seen from the following:

- Funke et al. discloses and claims a particular type of (1) microporous crystalline alumina silicates (e.g., zeolites) or (2) microporous crystalline alumina phosphates, ALPO, or silicaaluminaphosphates, SAPO, or Mobile Crystalline Material, MCM41, (e.g., molecular sieves) that are characterized by having a crystalline structure with a narrow distribution of pore sizes on a molecular scale, e.g., of about 0.54 nm or 5.4 Angstroms.
- Zeolite membranes or molecular sieves, e.g., ALPO, SAPO, or MCM41, of the type disclosed by Funke et al. have a fundamentally different physical structure than porous ceramic membranes, such as metal oxides, metal carbides and metal nitrides. The crystallographic structure of a zeolite defines the pore diameter in contrast to a metal oxide, e.g., alumina, wherein the pores are the interstices between the particles;
- Zeolite structures, such as the silicalites disclosed by Funke et al., typically are grown or synthesized hydrothermally from a gell and while extremely small pored structures may be routinely formed, the synthesis process leaves defects and separations or spaces (gaps) between crystals which can be larger than the pore sizes in the crystalline structures;

- That as such the problem facing the art and Funke et al. with producing acceptable microporous crystalline alumina silicates (e.g., zeolites) or the microporous crystalline alumina phosphates, ALPO, or silicaaluminaphosphates, SAPO, (e.g., molecular sieves) membranes with good separation capabilities for small molecules was not the need to trim the pore size of the crystals to a smaller pore size than achieved in the synthesis of the membrane materials (they already are characterized by pores of molecular dimensions) but was to find a way to seal the defects in individual crystals as well as microscopic gaps between individual crystals;
- That this is precisely what the Funke et al. process achieved by forming one or more layers 20 of additional structure on "one or more of the surfaces, 14, 16, 18 (such layers 20 can also be formed on the bottom or other surfaces) which layers are also porous enough to allow entry and passage of smaller molecules through the crystal lattice but which otherwise substantially block or clog the regions between the crystals ..." (see Column 6, lines 36-44);
- That as disclosed by Applicant the method for depositing one monolayer of an inorganic compound, e.g., alumina, achieves an effective reduction in mean pore diameter of the inorganic membrane product of a thickness of approximately one molecule of the inorganic compound which for gamma-phase alumina is a thickness of about 2.5 Angstroms;
- That based on this calculation if Funke et al. was, as suggested by the Examiner, concerned with depositing its monolayers on the surface of the pore walls of its zeolite or molecular sieve structures, which already has by the process of making same a pore size on the order of about 5.4 Angstroms, the pores would be substantially plugged and be rendered an ineffective molecular sieve membrane;
- That, in contradistinction to the Examiner's unsupported conclusion, Funke et al. process, does as Applicant argues, deposit the monomolecular layers on the surfaces of the zeolite or molecular sieves to effect a surface modification of the crystal surfaces and thereby alleviate the problem of larger molecules passing through the gaps between the crystals;
- That my conclusion is further supported in the Specification of Funke et al. at Column 9, lines 27-34 where there is discussed that one monomolecular layer deposited according to their invention is "formed around or over pore openings 24 in the crystals." There is no mention or showing in the drawings of the monomolecular layer being deposited within the pores of the membrane.
- That while Funke et al. does teach that their process can also decrease the effective size of the diameters of the pores the reduction is effectuated by reducing the diameter of the pore openings (not the internal diameter of the pores as Applicant does with its inorganic membrane) by the layer 20 covering the top

surface, as well as other exposed surfaces 16, 18 sufficiently to block or inhibit larger molecules from flowing through the membrane where the layer covering the surface does not substantially inhibit entry of the smallest molecules, e.g., nitrogen, helium or hydrogen. (See Specification Column 6, lines 45-56)

- That the only technically correct reading of the disclosure of Funke et al. patent is that their process is a surface modification of zeolite or molecular sieves of the type ALPO, SAPO, or MCM41 wherein a very thin monomolecular layer is deposited onto the surfaces of the membranes to block or partially block regions between the zeolite or molecular sieve crystals in the membranes without blocking or substantially affecting or decreasing effective pore size and molecular transfer through the respective crystals.
- That such teaching or disclosure does not read, as the examiner asserts, on Applicant's claims;
- That Funke et al. does not, contrary to the Examiner's unsupported statement, teach that the membrane, in addition to zeolites, may be "any other inorganic crystalline membrane that has surface hydroxyl groups." Their teaching is limited to a particular narrow class of molecular sieves, e.g., ALPO, SAPO, or MCM41, which are structurally similar to the zeolites in that they have a crystalline structure with a narrow pore size distribution on a molecular scale, i.e., of about 5.4 Angstroms.
- That in direct contrast, ceramic inorganic membranes, such as an alumina membrane disclosed and claimed by Applicant, typically for the smallest pore size available commercially will have a pore size, i.e., average pore diameter, of about 40 Angstroms and are unsuited as a molecular sieve.
- That Applicants' process overcame this problem by conducting successive cycles of depositing one monolayer at a time within the pores or interstices between the particles that make up the matrix material particles to reduce the mean pore diameter to below about 5 Angstroms, which required at least four cycles to achieve this extremely small molecular sieving pore size;

That as noted above he has carefully read and understands the Butler et al. patent cited by the Examiner against applicants' claims 2-24 and notes that it is a process for preparing a composite sheet comprised of a porous inorganic membrane, such as alumina and a microporous inorganic film, such as gamma-alumina, overlaying a surface of the membrane with the average pore size of the microporous film being from 0.5 to 30 nm. The inorganic film, for example, may be formed by applying a colloidal sol, which does not penetrate into the pores of the membrane, of an inorganic material to the membrane, and subsequently drying by heating to form the composite ultrafiltration membrane.

That it would not have been obvious from the teaching of Funke et al. in view of Butler et al. to use the metal oxide as the ceramic material

in Funke et al. as the Examiner has concluded with any reasonable expectation of success. As noted above, the Examiner is in error in his statement that Funke et al. teaches the art recognized suitability of using other ceramic membranes. The teaching of Funke et al. is limited to a particular narrow class of molecular sieves, e.g., zeolites and ALPO, SAPO, or MCM41, which are structurally similar to the zeolites in that they have a crystalline structure with a narrow pore sizes on a molecular scale, i.e., of about 5.4 Angstroms. As such, the membranes of Funke et al. have a fundamentally different physical structure than porous ceramic membranes, such as metal oxides, and pose a unique problem in the art, i.e., a way to seal the defects in individual crystals as well as microscopic gaps between individual crystals, that are not found with the metal oxides of Applicant's invention. There simply is not any hint or suggestion found in Funke et al. that wholly different types of materials, such as the metal oxide membranes disclosed and claimed by Applicant, could be substituted for their zeolite or molecular sieve materials with any reasonable expectation of success to prepare molecular sieve membranes.

That as noted above he has carefully read and understands the Levy et al. patent cited by the Examiner against Applicants' claims 2-24;

That as noted above he has read the Examiner's further rejection of Applicant's claims over Funke et al. in view of Levy et al. wherein the Examiner stated that Funke et al. does not explicitly disclose a gamma alumina or alumina membrane. The Examiner concluded, however, because Levy et al. discloses that it is desirable to decrease the pore size of alumina membranes by depositing inorganic compounds thereon, it would have been obvious to have coated an alumina membrane by the process of Funke et al. with a reasonable expectation that doing so would successfully provide an alumina membrane having an adjusted pore size to tailor its filtration properties;

That there is no teaching in Funke et al. in view of Levy et al. that would have motivated me with a reasonable expectation of success to use the Funke et al. process, which teaching is limited to modifying zeolite or molecular sieves of a similar crystallographic structure having a pore size of about 5.4 Angstroms, to coat a fundamentally different type of structure, such as an alumina membrane, that typically has an average pore size of about 40 Angstroms which makes them unsuited as a molecular sieve, to provide an alumina membrane having an adjusted pore size that is at least as small as 5 Angstroms.

That I am aware willful false statements and the like are punishable by fine or imprisonment, or both, (18 USC 1001) and may jeopardize the validity of this application or any patent issuing therefrom.

Further declarant sayeth not.

Roddie R. Jenkins
Roddie R. Jenkins, Ph.D

Feb. 1, 2006
Date